

PARTICULARS OF THERMALLY STIMULATED GAS-RELEASE FROM SILICA GLASS FIBER

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It is shown that under heating in air to 1100°C the mass of silica fiber decreases by approximately 11%. Primarily water is released into the gas phase. Hydrocarbons, carbon oxides, and molecular hydrogen were found in low concentrations in the gas phase in addition to water. The appearance of hydrocarbons could be due to molecules which are adsorbed on the fiber surface at the time the fiber is made. The release of water at high temperature is due to the destruction of silanol groups.

Key words: silica fiber, structure of fibers, x-ray phase analysis, thermogravimetric analysis, IR spectroscopy.

It is known that water is present in different materials based on silicon dioxide in the form of isolated H₂O molecules, in the form of H₂O molecules bound by hydrogen bonds, and in the form of silanol groups (Si–OH), which can exist in an isolated form but can also be bound by hydrogen bonds with water molecules and with one another [1–3]. Aside from SiO₂, commercial glass contains other components which are introduced during glassmaking, are sorbed from air during storage, or are used in the fabrication of the final articles. When such articles are used at high temperatures, not only water but also other adsorbed or weakly bound molecules as well as products of their thermal destruction into the gas phase can be released into the gas phase.

The present article gives data on the quantitative and qualitative composition of the gases released during heating of silica fibers, which are manufactured in Russia by a commercial method. Silica fibers are a multifunctional high-temperature and chemically stable material [4]. The production of silica fibers is based on the selective solubility (leaching) of individual oxides from certain silicate glasses with the simplest and complex compositions when they are exposed to acid solutions. As a result, the fiber is enriched with silicon oxide, whose content depends on the composition of the initial glass. The leaching capability of silicate glasses and fibers is due to the presence of structural silicon–oxygen network of the glass, remaining unchanged during extraction.

Domestic silica fibers are obtained on the basis of glass with sodium-aluminosilicate composition containing the following (wt.%): 94.0–96.0 SiO₂, 3.5–4.0 Al₂O₃, to 2.0 impurities (Na₂O, CaO, MgO, and others) [5].

After leaching, washing, and drying silica fibers have a porous hydrated structure [6]. These fibers are promising for use as heat-insulation material and carriers of catalysts. In many cases the fibers are used at high temperatures — to 1000°C. The gases released in this case can have a serious effect on, for example, the flow of a catalytic reaction.

In the present work, mass-spectrometry was used to study the composition of the gases formed when a silica fiber is heated in temperature intervals from room temperature to 650°C. The method is highly sensitive and makes it possible to detect molecules which are present at low concentrations in the gas. The data obtained are of interest not only as a characteristic of the particular object but they can be used to predict the behavior of other articles with a high content of silicon oxide on heating.

The primary certification of the silica fiber was done by means of x-ray phase analysis, thermogravimetric analysis (TGA), and IR spectroscopy.

DESCRIPTION OF EXPERIMENT

The composition of the silica fiber for preparing the experimental sample includes the following components (wt.%): 95.5 SiO₂, 3.6 Al₂O₃, 0.25 Na₂O, and 0.20 K₂O.

The diffraction patterns of the powders of glass fibers comminuted in a mortar were measured at room temperature

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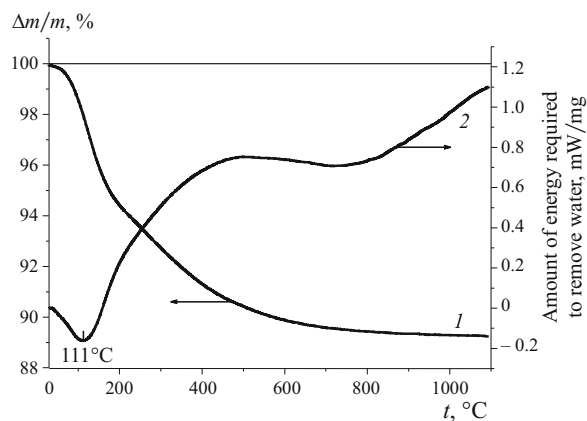


Fig. 1. Results of thermogravimetric analysis of the experimental sample of a KV-11 sample: 1) mass loss curve; 2) differential scanning calorimetry curve (DSC).

with a DRON ADP-01 diffractometer using monochromatic CuK_α radiation.

Thermogravimetric analysis (TGA) of weighed portions 10 mg was performed in air using a Netzsch STA 409 simultaneous thermal analyzer at temperatures ranging from 25 to 1100°C and with heating rate 10 K/min.

The IR spectra were recorded with a Perkin Elmer Spectrum 100 Fourier spectrometer with an UATR attachment.

The mass spectra of the gases released by glass fibers when heated in vacuum were recorded with an MI 1201V mass spectrometer. In this experiment a weighed amount of fiber (400 – 500 kg) was placed in a quartz ampul of a pyrolyzer, which was connected through a fine-regulation valve with a system for introducing the analyte gas into the mass spectrometer. The weighed portion placed into a quartz ampul was evacuated for 1 day to pressure approximately 2×10^{-5} Pa. This procedure is necessary to remove weakly bound impurities from the sample. After evacuation the ampul was isolated from the vacuum system, heated to a prescribe temperature T_1 , and held at this temperature for 3 h. Then the fine-regulation valve was opened and mass-spectrometric analysis of the gas collected in the ampul at this state of heating was performed. At the completion of the analysis the sample in the quartz ampul at temperature T_1 was once again evacuated to high vacuum and the valve was closed. The second sampling of the gas phase was performed at temperature T_2 for 3 h. There could be several such steps in the analysis, and $T_1 < T_2 < \dots < T_n$. The mass spectra were recorded in the interval $1 \text{ amu} \leq m/z \leq 250 \text{ amu}$, where m is the atomic mass, z is the ion charge, and m/z is the atomic unit of mass (amu), or the dalton.

RESULTS AND DISCUSSION

The sharp peaks characteristic for crystalline solid bodies are not present in the x-ray diffraction pattern of the experi-

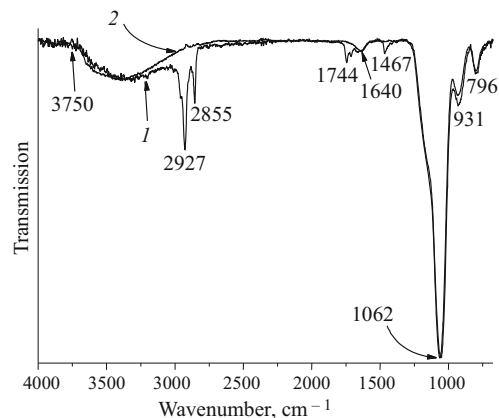


Fig. 2. IR spectra of the experimental fiber (1) and powder (2), obtained by comminution of the fiber.

mental glass fiber. There is only a wide halo in the region $11 < 2\Theta < 33^\circ$ with a maximum at approximately $2\Theta = 21^\circ$. Therefore, the silica glass fiber in the initial state is x-ray amorphous.

Figure 1 shows the curve of the loss of mass of the sample heated at the rate 10 K/min in air. The largest losses are observed from 100 to 600°C. The total loss of mass on heating to 1100°C is 10.75%, and after heating to 800°C the sample mass essentially stabilizes. A quite sharp heat absorption peak at 111°C is observed on the differential scanning calorimeter (DSC) curve; in the authors' opinion that this peak is due to the evaporation of the equilibrium moisture.

The IR spectra of the experimental sample (Fig. 2) were obtained in two ways using a frustrated total internal reflection (FTIR) attachment: 1) by pressing the initial fibers to a Ge crystal of the attachment; 2) by depositing on the crystal of the attachment a powder obtained by comminution (immediately prior to measurement) of the experimental fiber in a mortar. It is evident that the signal/noise ratio for sample 2 is higher even though both spectra were obtained under identical conditions. The intensity loss is related with the fact that micron fibers cannot cover the entire surface of the crystal of the attachment compactly as can a fine powder. Nonetheless, the shape of the strongest asymmetric absorption band (AB) with a peak at 1062 cm^{-1} and a shoulder at approximately 1200 cm^{-1} is the same for both spectra. It is well known that the AB is due to the stretching vibrations of the Si–O–Si bonds [7].

The authors attribute the additional peaks (2927, 2855, 1744, and 1467 cm^{-1}) which are present in the spectrum of the initial fiber to molecules which were adsorbed on the fiber surface during fabrication. It is evident that the AB at 2927 and 2855 cm^{-1} are associated with stretching vibrations of C–H bonds of aliphatic hydrocarbons. Thus, molecules of hydrocarbons and/or products of their thermal decomposition can be present in the gases which will be released from the sample on heating.

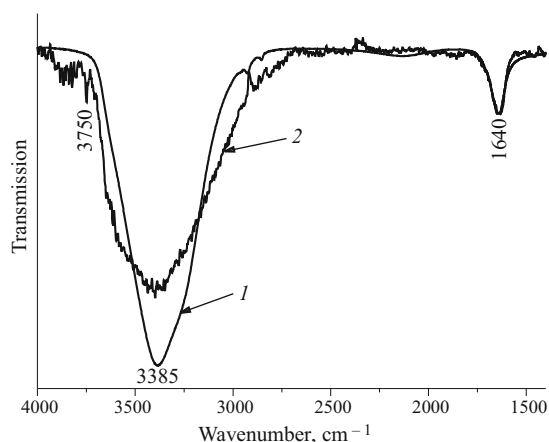


Fig. 3. IR spectra of the experimental fibers (1) and water (2).

We shall now analyze, using published data, the origin of other ABs which are present in the spectrum of silica glass fiber. The AB at 931 cm^{-1} is usually associated to stretching vibrations of the Si–O bonds of Si–OH groups [7]. The change of the AB intensity during grinding signifies that the ratio of the concentration of the Si–OH fragments to the concentration of Si–O–Si fragments is higher on the surface of the fiber than in the volume. As is well known, the AB at 1635 cm^{-1} is due to the deformation vibrations of the water molecules. Grinding makes virtually no change in the intensity of this AB. Here the profile of AB in the region of the stretching vibrations of O–H bonds changes somewhat. Taking account of the data from [8] it would seem that the concentration of OH groups with strong hydrogen bonds is higher on the surface of the fibers than in the volume. Moreover, a narrow AB at 3750 cm^{-1} due to the isolated (no hydrogen bonds) SiO–H groups (Figs. 2 and 3) is also seen in the spectrum of ground fibers.

The presence in the sample of a glass-forming additive — aluminum oxide — is manifested in the spectrum as a small shift of the strongest AB by 6 cm^{-1} in the direction of lower wave numbers. The AB at 930 cm^{-1} shifts in the direction of low wave numbers by 2 cm^{-1} . This was established by comparing the spectrum of the experimental sample (see Fig. 2) with the spectrum of a specially prepared sample with no Al_2O_3 . Separate peaks which could be associated to a phase of Al_2O_3 were not found in the spectrum of the experimental sample. The spectrum of amorphous aluminum oxide, which forms in air on the surface of metallic aluminum, was obtained for comparison. It was established that the strongest band in this spectrum is the wide AB at 720 cm^{-1} . Such an AB is not present in the spectrum of the experimental sample.

The IR spectrum of water is well known. But there are no publications where the spectra of water and silica are compared in a single, clear figure. In Fig. 3 the spectrum of water and powder of the experimental silica glass fiber are matched with respect to the peak intensity of the AB corresponding to

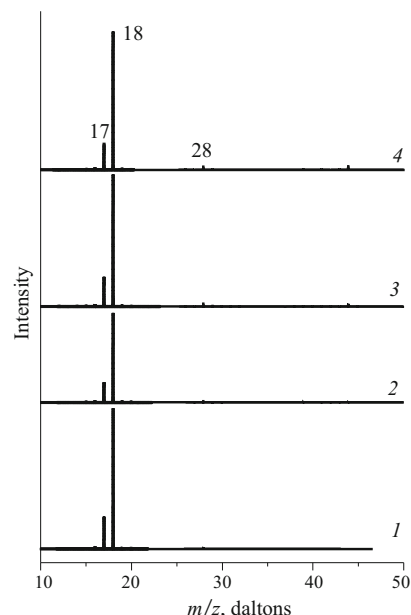


Fig. 4. Mass spectra of gases released by the experimental sample in the temperature intervals: 23 – 200 (1), 200 – 300 (2), 300 – 400 (3), and 400 – 650°C (4).

the deformation vibrations of the water molecule. As one can see from the figure, the half-width of the AB of the stretching vibrations in the spectrum of the glass fiber is larger than in the water spectrum. Exactly the opposite situation obtains for AB of the deformation vibrations. This is because in the glass spectrum not only water molecules but also silanol groups contribute to the intensity of the AB of the stretching vibrations. For silanol groups the effective force constant of the O–H bond show a very large spread. In the literature this spread is often attributed to the presence in these groups of a different hydrogen bond strength: the AB for groups with a weak hydrogen bond lies in the range $3600\text{--}3750\text{ cm}^{-1}$, while the AB for groups with a strong bond lies at $3400\text{--}3500\text{ cm}^{-1}$ [6]. The tail on the side of the lower wave numbers relative to the indicated range is customarily attributed to OH groups with a very strong hydrogen bond.

Since the AB of the deformation vibrations are due to water molecules only, it follows from an analysis of the shape of the AB that at least for some water molecules in the silica matrix the hydrogen bonds are weaker than those for molecules in the liquid phase.

It also follows from the comparison made that the ratio of the intensities of the absorption bands of the stretching and deformation vibrations of water molecules changes on transitioning from the liquid phase to the SiO_2 matrix. This observation is important for the quantitative estimates of the water content in glasses based on IR-spectroscopic data.

In the mass spectra of gases which are released by a silica glass fiber in all experimental temperature intervals, the main peak is the one with $m/z = 18$ amu, which corresponds to the molecular ion $[\text{H}_2\text{O}]^+$ (Fig. 4). The next weakest peak

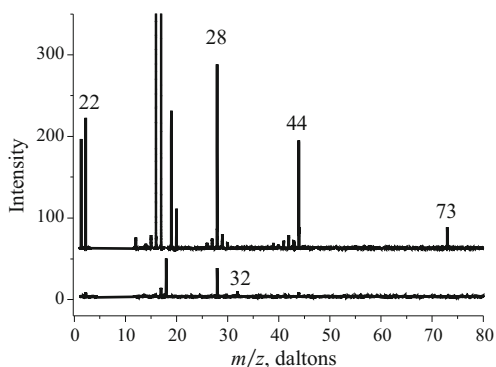


Fig. 5. Mass spectrum of the residual gases (bottom) and mass spectrum of the gas released by the experimental sample in the temperature intervals 23 – 200°C (top). For clarity of comparison, the top spectrum is shifted by 60 arb. units and its intensity is bounded by the value 300 arb. units.

($m/z = 17$ amu, ion $[\text{HO}]^+$) arises because of the fragmentation of the water molecule in the ionic source. Of the other peaks with appreciable (against the background of water peaks) intensity the peaks with $m/z = 28$ and 44 amu should be noted; these peaks are usually ascribed to the ions $[\text{CO}]^+$ and $[\text{CO}_2]^+$, respectively. As regards the hydrocarbon contaminants observed on fiber surfaces in a study of the IR spectra, on the basis of intensity the strongest ones are less than 1% of the intensity of the water peak. Since we are talking about peaks with a low intensity, the question of the spectrum of the residual gases arises naturally.

Figure 5 compares the mass spectrum of residual gases with the spectrum of gases which were released when a glass fiber was heated to 200°C. It is evident that the main peak in the residual-gas spectrum is once again the peak corresponding to the ion $[\text{H}_2\text{O}]^+$. However, its intensity is less than 0.2% of the intensity of the peak in the spectrum being compared. Only the peak with $m/z = 32$ amu (ion $[\text{O}_2]^+$) in the residual-gas spectrum is of comparable intensity with the peak in the spectrum of the gas released by the fiber (9 and 6 arb. units, respectively). The low intensity of this peak in the spectrum of the gases studied means that in the indicated temperature range molecular oxygen is not released from the glass fiber. The excess of the intensity of the peak with $m/z = 32$ amu above the intensity of the peak in the residual-gas spectrum is observed only in the temperature interval 300 – 400°C.

The hydrocarbon contaminants manifest in the mass spectrum as two groups of peaks, corresponding to C2 ($m/z = 25 - 29$ amu) and C3 ($m/z = 39 - 43$ amu) hydrocarbons. A characteristic feature of these groups is the fact that within the groups the distance between the nearest peaks is 1 amu, which corresponds to detachment of one hydrogen atom. To establish the presence of methane in the spectrum, a high-resolution spectrum was obtained in the region $m/z = 16$ amu. The result of this experiment is presented in Fig. 6. It is evident that two peaks are present in this range, one at

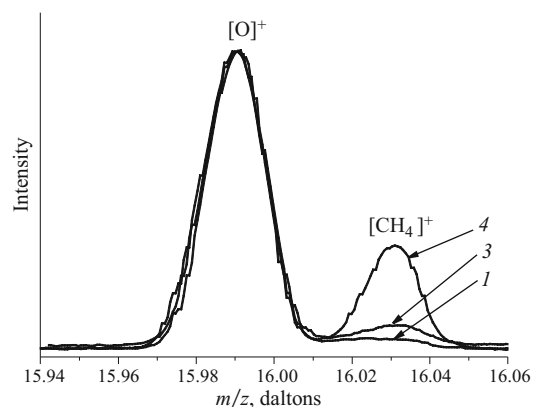


Fig. 6. Fragments of the mass spectra of the gases released by the experimental sample in the temperature intervals: 23 – 200 (1), 300 – 400 (3), and 400 – 650°C (4).

$m/z = 15.99$ amu and 16.03 mm, which are due to the ions $[\text{O}]^+$ and $[\text{CH}_4]^+$. Accurate values of the mass of these ions are 15.99491502 and 16.03130076, respectively [10]. As the annealing temperature increases, the relative intensity of the $[\text{CH}_4]^+$ peak increases.

Finally, a peak with $m/z = 2$ amu (ion $[\text{H}_2]^+$) is present in the spectrum of the gases above the glass fibers; the intensity of this peak is comparable to that of the peaks with $m/z = 28$ and 44 amu (see Fig. 5). The intensity of the peak with $m/z = 2$ amu decreases with increasing temperature. Since a molecular bleeding regime is realized in the spectrum, the source of the molecular hydrogen should be sought in the glass fiber.

It was established that the intensity of the peaks with $m/z = 28$ and 44 amu increase with temperature, and the intensity of the peak with $m/z = 44$ amu increases with increasing rates. In the temperature interval the peak with $m/z = 44$ amu already is stronger than the peak with $m/z = 28$ amu. If it is assumed that these peaks are due to the carbon oxides, which are formed with oxidation of the hydrocarbon contaminants, then it is unclear why the concentration of carbon oxides increases in parallel with the increase of the methane concentration. The increase of the intensity of the peaks with $m/z = 28$ and 44 amu with temperature could also be explained by the formation of the oxide SiO , which likewise appears in the mass spectrum in the form of the peaks with $m/z = 28$ and 44 amu. However, the resolving power of our instrument does not permit distinguishing the peaks due to $[\text{SiO}]^+$ and $[\text{CO}_2]^+$.

CONCLUSIONS

It was established that on heating in air the mass of a silica glass fiber can decrease by more than 11%. In the process, primarily water is released into the gas phase. Aside from water, hydrocarbons, carbon oxides, and molecular hy-

drogen were also found in the gas phase. The appearance of hydrocarbons could be due to hydrocarbon molecules adsorbed on the fiber surface during fabrication or storage.

The results obtained show that when silica materials are used as heat insulation at high temperatures the compounds that could affect the environment are not released. Any effect of water vapor on protected articles can be eliminated by preliminary heat-treatment of the silica materials.

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